The origin of $^{12}CH_2D_2$ depletions in microbialgenic methane gases

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The abundances of $^{12}CH_2D_2$ and $^{13}CH_3D$ relative to stochastic distributions of methane isotopologues are proving to be useful tracers of the provenance of methane gas. A striking feature of gases produced by microbial methanogenesis is the depletion in $^{12}CH_2D_2$ of order 20 to 50 ‰ relative to thermodynamic equilibrium or stochastic values [1,2]. The precise origin of this apparent signature of microbial methane production is relevant to its robustness as an indicator of microbialgenic CH_4 gas in general.

We investigated the $\Delta^{12}CH_2D_2$ and $\Delta^{13}CH_3D$ (‰ relative to stochastic) of CH_4 gas produced by metabolic decomposition of methylphosphonate (CH_5O_3P) by a uqibuitous heterotroph, *Pseudomonas stutzeri*. The isotopic effects of the reaction can be regarded to first order as a simple bimolecular reaction between the medium H_2O and the CH_3-group from CH_5O_3P. The δD and $\delta^{13}C$ of the CH_3 are known. By varying reactant water δD, we isolated the source of the $\Delta^{12}CH_2D_2$ isotope clumping effect.

Our results indicate that the great majority of the $\Delta^{12}CH_2D_2$ signature of methane produced by *P. stutzeri* is the result of the difference in D/H between the water and reactant-CH_3. The match between predicted and measured isotopologue abundances is a clear indication that the "combinatorial" effect described previously [2-4] is the primary cause of the highly negative $\Delta^{12}CH_2D_2$ values and invariant $\Delta^{13}CH_3D$ values for the CH_4 produced by *P. stutzeri* in these incubations. For example, with water δD = -64‰ (VSMOW) and $\delta^{13}C$ $\delta^{13}C$ of CH_5O_3P = -100‰ (VPDB), the combinatorial effect predictions (and measured values) for methane δD, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ are −304‰ (−308‰), −0.33‰ (1.3‰) and −41.8‰ (−42.9‰), respectively. For water with δD = 1500 ‰ the predicted (measured) δD, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values for methane are −191.5‰ (−192.4‰), −0.6‰ (0.4‰), and −2.0‰ (0.3‰), respectively. The $\delta^{13}C$ is ~ −100‰ in all cases. Similar results for a wide variety of water D/H measurements illustrates the dominance of the combinatorial effect.

Any reaction involving hydrogen from reservoirs with disparate D/H ratios could in principle cause similarly low $\Delta^{12}CH_2D_2$ values.

[1] Young et al. (2017) *GCA* 203; [2] Yeung et al. (2015) *Science* 348; [3] Yeung (2016) *GCA* 172; [4] Röckmann et al. (2016) *Scientific Reports*.